

Chemical Kinetic Study of Toluene Oxidation

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Abstract

A study was performed to elucidate the chemical-kinetic mechanism of combustion of toluene. A detailed chemical-kinetic mechanism for toluene was improved by adding a more accurate description of the phenyl + O₂ reaction channels, toluene decomposition reactions and the benzyl + O reaction. Results of the chemical kinetic mechanism are compared with experimental data obtained from premixed and nonpremixed systems. Under premixed conditions, predicted ignition delay times are compared with new experimental data obtained in shock tube. Also, calculated species concentration histories are compared to experimental flow reactor data from the literature. Under nonpremixed conditions, critical conditions of extinction and autoignition were measured in strained laminar flows in the counterflow configuration. Numerical calculations are performed using the chemical-kinetic mechanism at conditions corresponding to those in the experiments. Critical conditions of extinction and autoignition are predicted and compared with the experimental data. Comparisons between the model predictions and experimental results of ignition delay times in shock tube, and extinction and autoignition in nonpremixed systems show that the chemical-kinetic mechanism predicts that toluene/air is overall less reactive than observed in the experiments. For both premixed and nonpremixed systems, sensitivity analysis was used to identify the reaction rate constants that control the overall rate of oxidation in each of the systems considered. Under shock tube conditions, the reactions that influence ignition delay time are H + O₂ chain branching, the toluene decomposition reaction to give an H atom, and the toluene + H abstraction reaction. The reactions that influence autoignition in nonpremixed systems involve the benzyl + HO₂ reaction and the phenyl + O₂ reaction.

Introduction

Alkylated benzenes are an important class of hydrocarbons because they comprise a significant portion of gasoline and diesel fuels. Knowledge of the oxidation chemistry of alkylated benzenes is needed in developing predictive models that can treat autoignition, and premixed and nonpremixed burning of transportation fuels in internal combustion engines. Toluene (C₆H₅CH₃) has one of the simplest molecular structures of the alkylated benzenes and is a reasonable starting point for the development of detailed chemical-kinetic reaction mechanisms for alkylated benzenes. Much previous work has been done on the oxidation of toluene. Several research groups have developed detailed chemical-kinetic reaction mechanisms for toluene. Most recently, Klotz et al. [1] supplemented the toluene mechanism of Emdee et al. [2] to improve the predictions for the intermediates 1,3 butadiene, acetylene and benzaldehyde. Zhong and Bozzelli [3-5] developed a more accurate description of radical additions

to cyclopentadiene and associations with cyclopentadienyl radical; they included these reactions in a detailed chemical-kinetic mechanism for toluene that they developed. Lindstedt and Maurice [6] developed a very comprehensive toluene mechanism whose predictions they compared to experimental results from counterflow diffusion flames, plug flow reactors, shock tubes and premixed flames. Emdee et al. [2] developed a detailed chemical-kinetic mechanism for toluene that was benchmark for many years.

There are quite a few experimental studies of toluene oxidation whose data are very useful for mechanism validation. Several experimental studies of toluene oxidation in a flow reactor were performed at Princeton University [1, 2, 7, 8]. Ignition of toluene in a rapid compression machine was performed by Griffiths et al. [9] and by Roubaud et al. [10]. Their rapid compression machine results show that toluene oxidation chemistry lacks the two stage ignition observed in paraffinic fuels. Experimental data for the critical conditions of autoignition of toluene in the counterflow configuration are given in Ref. [11]. Using this experimental data, overall chemical-kinetic rate parameters that characterize the rate of one-step overall reaction between fuel and oxygen were obtained [11]. The present work offers new results for shock tube ignition of toluene and new results for extinction under nonpremixed conditions. These experiments provide additional data for validating chemical-kinetic mechanisms for toluene. In particular, the results under nonpremixed conditions highlight the influence of strain on autoignition and extinction.

Experimental

Shock tube experiments

The experiments were performed in a stainless steel 78 mm diameter shock tube at DCPR-CNRS-NANCY. The reaction and driver parts were separated by two terphane diaphragms, which were ruptured by suddenly decreasing the pressure in the space separating them. The driver gas was helium and the reacting mixture was diluted in argon. The incident and reflected shock velocities were measured by four piezo-electric pressure transducers located along the reaction section. The state of the test gas behind the incident and the reflected shock waves was derived from the value of the incident shock velocity by using classical, one-dimensional, shock equations of mass, momentum, and energy conservation applied to an ideal gas.

The pressure profile displayed three rises, which were due to the incident shock wave, the reflected shock wave and the ignition, respectively. The onset of ignition was, however, most accurately detected by OH radical emission at 306 nm through a quartz window with a photomultiplier fitted with a monochromator at the end of the reaction section. The last pressure transducer was located at the same place along the axis of the tube as the quartz

window. The ignition delay time was defined as the time interval between the pressure rise measured by the last pressure transducer due to the arrival of the reflected shock wave and the rise of the optical signal by the photomultiplier up to 10% of its maximum value. The ignition delay times were corrected for blast wave effects by adding $3 \mu\text{s}$ to the measured time [12].

Oxygen and helium were purchased from Air Liquide-Alphagaz and toluene was provided by Aldrich (purity: 99.8%). The toluene concentration in the reactants was kept constant at 1.25%. The values of equivalence ratio, ϕ , examined were 0.5, 1.0 and 1.5. The reflected shock pressures and temperatures ranged from 8.0 to 9.4 atm and 1300 to 1900 K, respectively.

Experiments under Nonpremixed Conditions

Experiments under nonpremixed conditions were carried out in the counterflow configuration. Figure 1 shows a schematic illustration of the counterflow configuration. Steady, axisymmet-

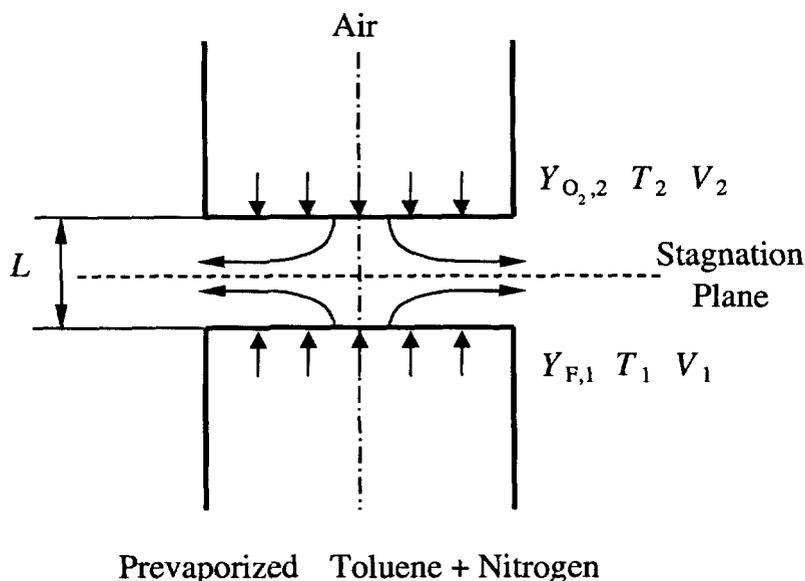


Figure 1: Schematic illustration of the counterflow configuration.

ric, laminar flow of two counterflowing streams toward a stagnation plane is considered. In this configuration a fuel stream made up of prevaporized toluene and nitrogen is injected from the fuel-duct, and an oxidizer stream of air is injected from the oxidizer-duct. These jets flow into the mixing layer between the two ducts. The exit of the fuel-duct is called the fuel boundary and the exit of the oxidizer-duct the oxidizer boundary. The mass fraction of fuel, the temperature, and the component of the flow velocity normal to the stagnation plane at

the fuel boundary are represented by $Y_{F,1}$, T_1 , and V_1 , respectively. The mass fraction of oxygen, the temperature, and the component of the flow velocity normal to the stagnation plane at the oxidizer boundary are represented by $Y_{O_2,2}$, T_2 , and V_2 , respectively. The tangential components of the flow velocities at the boundaries are presumed to be equal to zero. The distance between the fuel boundary and the oxidizer boundary is represented by L .

In the experiments the momenta of the counterflowing reactant streams $\rho_i V_i^2$, $i = 1, 2$ at the boundaries are kept equal to each other. Here ρ_1 and ρ_2 represent the density of the mixture at the fuel boundary and at the oxidizer boundary, respectively. This condition ensures that the stagnation plane formed by the two streams is approximately in the middle of the region between the two boundaries. The value of the strain rate, defined as the normal gradient of the normal component of the flow velocity, changes from the fuel boundary to the oxidizer boundary [13]. The characteristic strain rate on the oxidizer side of the stagnation plane a_2 is presumed to be given by [13]

$$a_2 = \frac{2|V_2|}{L} \left(1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}} \right). \quad (1)$$

Equation 1 is obtained from an asymptotic theory where the Reynolds numbers of the laminar flow at the boundaries are presumed to be large [13]. Critical conditions of extinction are presumed to be given by the strain rate, $a_{2,e}$, and the mass fraction of fuel at the fuel boundary. Critical conditions of autoignition are presumed to be given by the strain rate, $a_{2,I}$, the temperature of the oxidizer stream, $T_{2,I}$, and the mass fraction of fuel and at the fuel boundary. The experiments were conducted at a pressure of 1.013 bar.

A detailed description of the burner is given elsewhere [11, 14]. The flow rates of gases were measured by computer-regulated mass flow controllers. The velocities of the reactants at the boundaries were presumed to be equal to the ratio of their volumetric flowrates to the cross-section area of the ducts. The temperature of the fuel stream and the temperature of the oxidizer stream at the boundaries were measured using thermocouples. The measured temperatures were corrected for radiative heat losses. The accuracy of the radiation-corrected temperatures is expected to be ± 25 K. A brief description of the experimental procedure is given here.

In the extinction experiments the temperature of the fuel stream, $T_1 = 378$ K, and the temperature of the oxidizer stream, $T_2 = 298$ K. The distance between the fuel boundary and the oxidizer boundary was $L = 10$ mm. At some selected value of $Y_{F,1}$ the flame was stabilized at $a_2 < a_{2,e}$. The strain rate was increased by increasing V_1 and V_2 until extinction was observed. Experimental results are shown later. Previous autoignition experiments were

conducted with the mole fraction of prevaporized fuel maintained at 0.15 [11]. The temperature at the fuel boundary, $T_1 = 378$ K. The distance between the fuel boundary and the oxidizer boundary was $L = 12$ mm. At a given strain rate and oxidizer temperature $T_2 < T_{2,I}$ the flow field was established. The temperature at the oxidizer boundary was gradually increased until autoignition took place. Experimental results are shown later.

Detailed Chemical-Kinetic Mechanism

The detailed chemical-kinetic mechanism for toluene was assembled by adding the toluene and benzene reaction mechanism of Zhong et al. [2–5] to the C₁-C₄ mechanism of Refs. [15] and [16]. The detailed chemical-kinetic mechanism is made up 349 species and 1631 reversible reactions. The entire mechanism will be available from our Web page (see Ref. [17]). The ultimate objective of this work is to add toluene as a fuel component to detailed chemical-kinetic mechanisms for alkanes that have been developed at Lawrence Livermore National Laboratories (LLNL) [18]. This combined alkane-toluene mechanism will provide a more complete mechanism for modeling combustion of gasoline or diesel fuels.

The toluene mechanism was improved in several ways. Rate constants of key reactions were estimated using Quantum RRK analysis to obtain $k(E)$ and master equation analysis [19] to evaluate pressure fall-off. Reactions analyzed included toluene decomposition reactions and the reaction of benzyl radicals with O atoms. The unimolecular decomposition of toluene giving benzyl + H was found to be an important reaction controlling shock tube ignition. The reaction of benzyl radicals with O atoms to give benzaldehyde + H is the primary path consuming benzyl under shock tube and flow reactor conditions.

The reaction rate constants for phenyl + O₂ system developed by Bozzelli et al. [19] were incorporated. These reaction channels included new products for which consumption reactions were added. The phenyl + O₂ rate constants were found to play an important role under counterflow-ignition conditions.

The rate constant for the initiation reaction (toluene + O₂ \rightleftharpoons benzyl + HO₂) was updated ($k = 9.3 \times 10^8 T^{1.301} \exp(-40939.0 \text{ cal}/RT) \text{ cm}^3/(\text{mol}\cdot\text{s})$) using one half the rate constant of allylic isobutene + O₂ [20]. Our estimate is 50 percent higher than the estimate of Walker [21] at 1000 K. Reactions to consume bicyclopentadiene were also added.

Comparisons between Numerical Calculations and Experiments

Shock Tube Comparisons

The ignition in the shock tube was simulated using the Senkin code [22] assuming constant volume combustion after the reflected shock passes through the mixture. The measured results are compared to predicted results in Fig. 2. In the experiments, 10 percent of the maximum

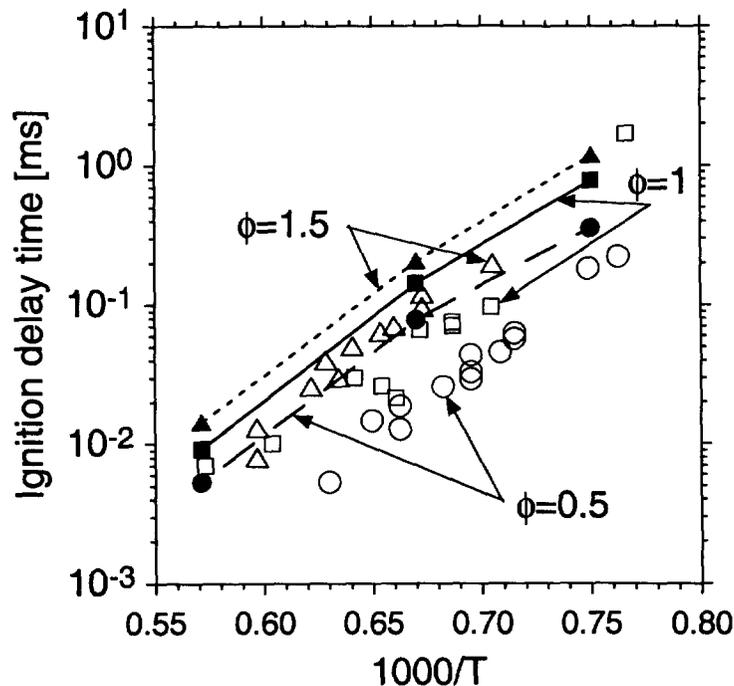


Figure 2: Predicted (lines and filled symbols) and measured (unfilled symbols) ignition delay times of toluene/ O_2 /Ar mixtures under shock tube conditions. (T = reflected shock temperature in Kelvin).

OH emission was used as an indication of ignition. The computed ignition delay time was obtained using the inflection in the temperature profile as an indication of ignition. When 10 percent of the OH maximum concentration was used in the calculations, almost identical results were obtained over the temperature range considered. We did not attempt to simulate OH emission. The predicted ignition delay times compared reasonably well with experimental values for the fuel-rich case, but were too long for the fuel-lean case.

Standard Senkin sensitivity analysis [22] was performed to determine the reaction rate constants that control the oxidation of toluene under shock tube conditions. The Senkin code

gives the change in species concentration for an incremental change in reaction rate constant. The OH radical concentration was chosen as an indicator of the overall reactivity of the system. An alternate choice of toluene concentration produced similar results. The sensitivity of OH concentration to a change in reaction rate constant is shown in in Fig. 3. The results are

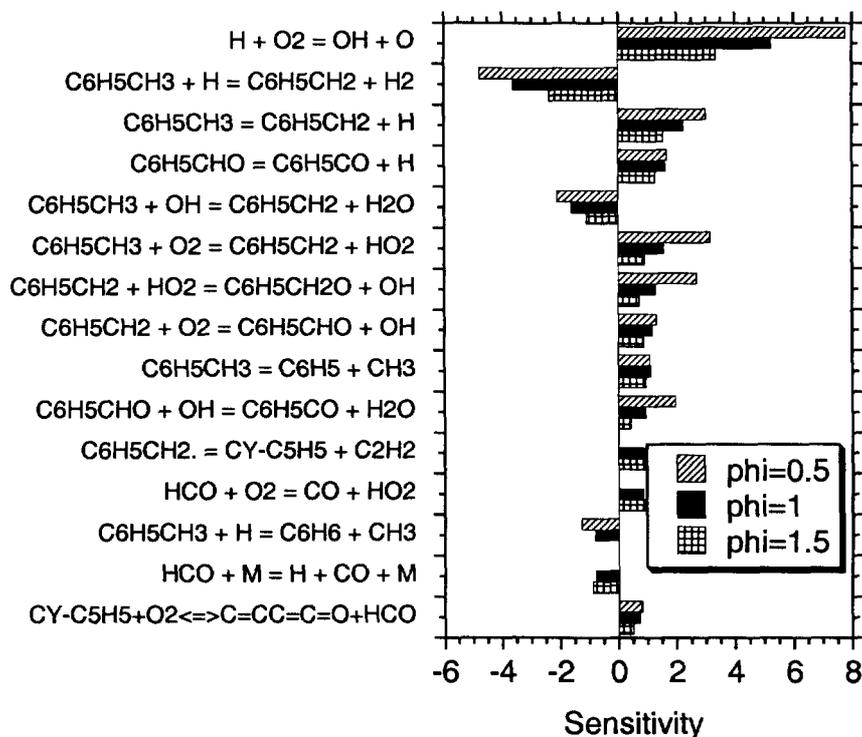
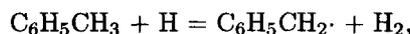


Figure 3: Sensitivity of the OH radical concentration to changes in individual rate constants under the shock tube conditions shown in Fig. 2 with $1000/T = 0.67$, where T is given in Kelvin.

shown when the toluene is about half consumed. Positive sensitivities indicate, an increase in rate constant increases the OH concentration and accelerates the overall rate of reaction, while negative sensitivities indicate an increase in rate constant decreases the OH concentration and retards the overall rate of reaction. The reaction giving the highest sensitivity is H + O₂ chain branching (Fig. 3). The sensitivities of the other controlling reactions can be understood in relationship to it. The abstraction reaction



removes H atoms that would otherwise lead to chain branching via H + O₂ so it exhibits a high negative sensitivity and retards ignition. We used the rate constant from Baulch et

al. [23]. This rate constant has an uncertainty of about a factor of 2 at 1700 K. The toluene decomposition channel,

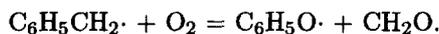


produces H atoms that can then lead to chain branching and thus exhibits a high positive sensitivity and accelerates ignition. This reaction was analyzed carefully with quantum RRK and master equation treatment because of its importance under shock tube conditions. The reaction $\text{C}_6\text{H}_5\text{CHO} = \text{C}_6\text{H}_5\text{CO}\cdot + \text{H}$ also produces H atoms and therefore exhibits a significant positive sensitivity. The inclusion of this reaction significantly improved the shock tube predictions at high temperature. The reaction of toluene with OH shows a large negative sensitivity and thus retards ignition. At fuel-lean conditions, the reaction $\text{C}_6\text{H}_5\text{CH}_3 + \text{O}_2 = \text{C}_6\text{H}_5\text{CH}_2\cdot + \text{HO}_2$ shows a high positive sensitivity. Further theoretical or experimental investigations of this reaction and the reaction of toluene with H atoms may help improve agreement with the shock tube experiments under fuel-lean conditions.

Flow Reactor Comparisons

The flow reactor was simulated using the Senkin code [22]. The predicted results are compared to the measurements of Klotz et al. [1] in Figs. 4 and 5. The results of the fuel profile look reasonable and the early appearance of the benzylaldehyde peak compared to the benzene peak is predicted. Many of the peak intermediate concentrations are predicted within a factor of two of the measurements, except for benzylaldehyde which is within a factor of three and 1,3-butadiene which is predicted to be in very low concentrations compared to the measurements.

Senkin sensitivity analysis [22] was performed to determine the reaction rate constants that control the oxidation of toluene under flow reactor conditions. The toluene concentration was chosen as an indicator of the overall reactivity of the system. The sensitivity of the toluene concentration at 135 ms to a change in reaction rate constant is shown in Fig. 6. At 135 ms, the initial toluene is about 48 percent consumed. Negative sensitivities indicate that the reaction accelerates the overall rate of reaction and positive sensitivities indicate the opposite effect. The reaction exhibiting the highest sensitivity is again the H + O₂ chain branching reaction. The second most sensitive reaction is the reaction of benzyl and O₂:



The rate constant of this reaction, $k = 5.30 \times 10^{13} T^{-1.07} \exp(-10840 \text{ cal}/RT)$, was taken from Zhong [4]. This reaction occurs through a 4-membered transition state where the terminal oxygen on the benzyl peroxy radical adds to the benzene ring.

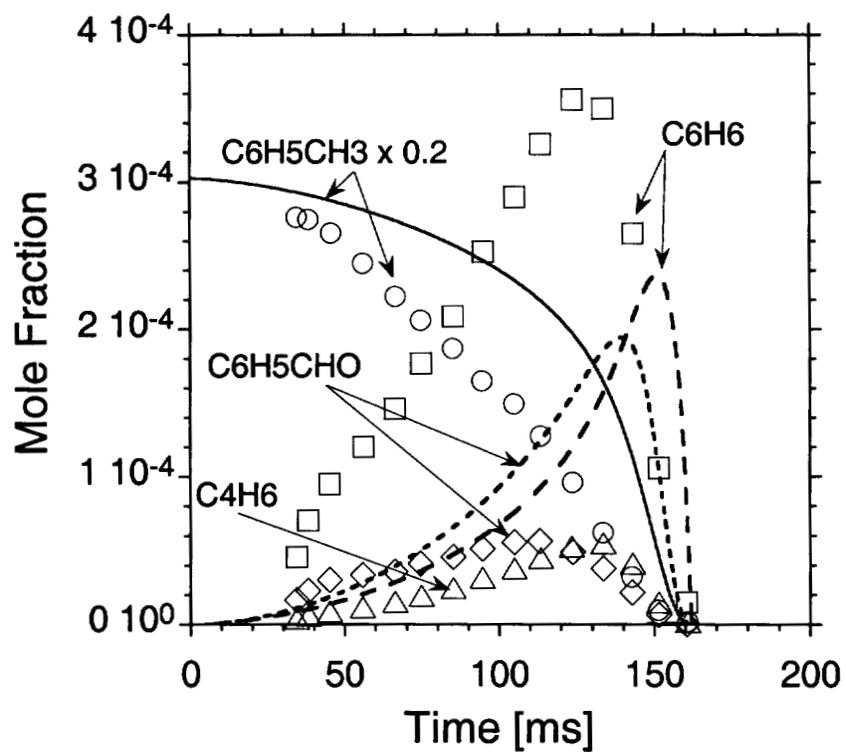


Figure 4: Predicted and measured concentration histories under flow reactor conditions. ($\phi = 0.76$, N_2 98 %, initial temperature = 1173 K, atmospheric pressure, time is residence time in flow reactor). The symbols represent measurements of Klotz et al. [1]. The lines are results of numerical calculations.

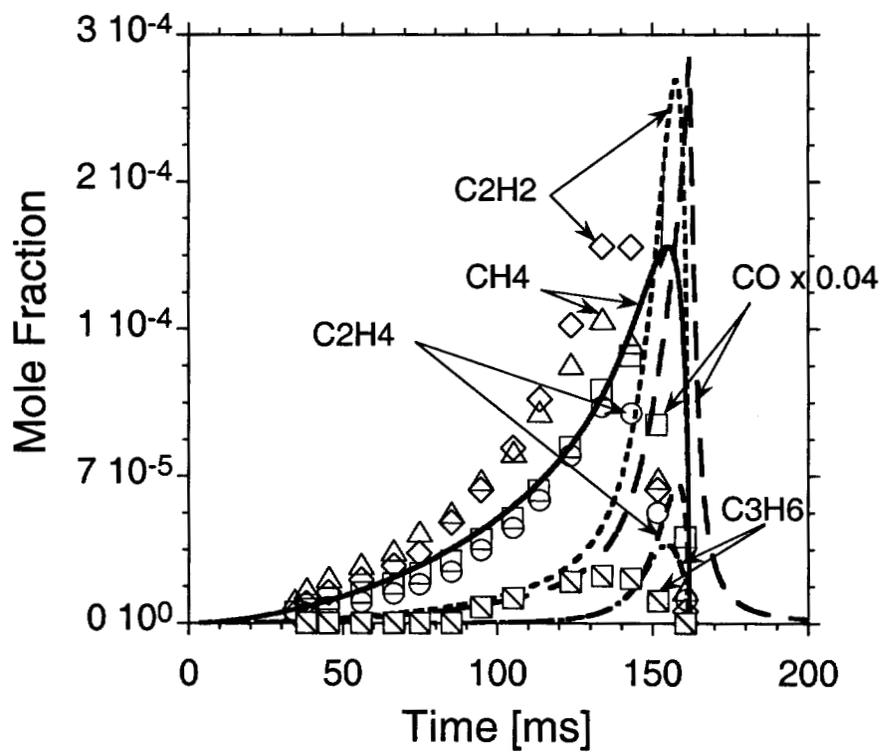


Figure 5: Predicted and measured concentration histories under flow reactor conditions. ($\phi = 0.76$, N_2 98%, initial temperature = 1173 K, atmospheric pressure, time is residence time in flow reactor). The symbols represent measurements of Klotz et al. [1]. The lines are results of numerical calculations.

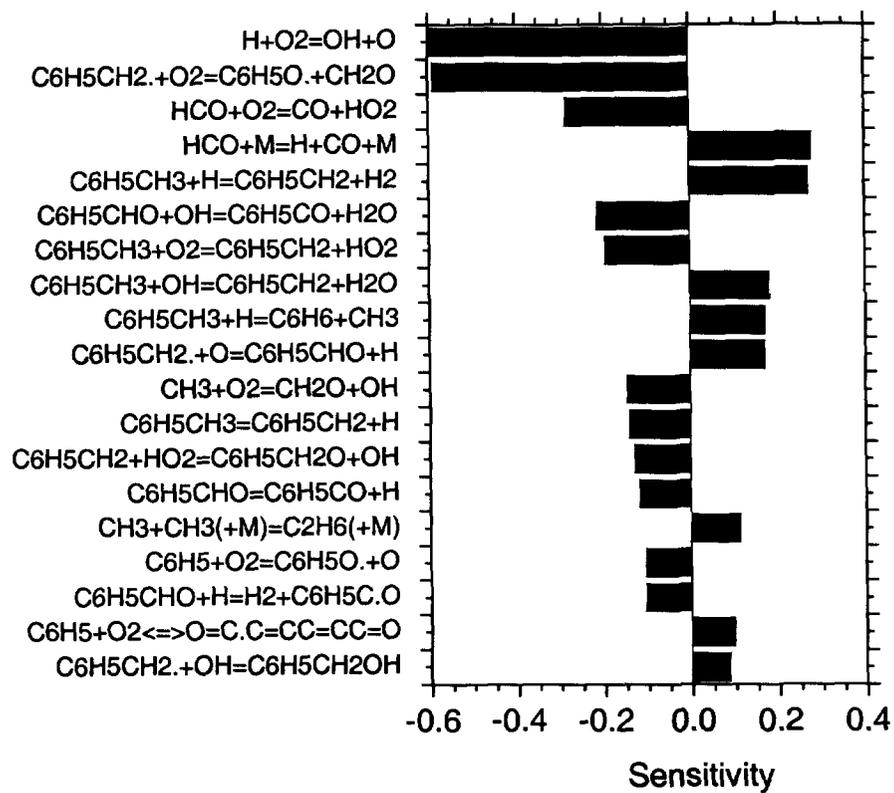
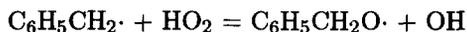


Figure 6: Sensitivity of the toluene concentration to changes in individual rate constants under flow reactor conditions. (equivalence ratio = 0.76, N_2 98 %, initial temperature = 1173 K, atmospheric pressure, residence time is 135 ms).

The $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$ reaction promotes fuel oxidation because it produces HO_2 radicals that react with benzyl radicals via,



a reaction with a negative sensitivity that also promotes fuel oxidation. The reaction of toluene with H atoms exhibits a positive sensitivity and retards the overall fuel oxidation rate, as seen under shock tube conditions.

Comparisons with Strained Laminar Flow under Nonpremixed Conditions

The detailed chemical-kinetic mechanism was tested by comparing computed results with experiments performed under strained, nonpremixed conditions. Numerical calculations were carried out using FlameMaster [24]. The formulation of the numerical problem is summarized elsewhere [24, 25]. At both ends of the computational domain, the mass fractions of the reactants and the normal components of the flow velocity were specified. The values of the tangential component of the flow velocity at both ends were set equal to zero (the so-called plug-flow boundary conditions). The characteristic strain rate at the stagnation plane was calculated using Eq. (1). Solutions could not be obtained with the 349 species detailed chemical-kinetic mechanism due to numerical "stiffness" problems. The detailed chemical kinetic mechanism was simplified using the NIST XSenkplot [26]. Simplified mechanisms were obtained under shock tube conditions and flow reactor conditions and combined to yield a 58 species mechanism made up of 221 reversible reactions. Any reaction in the detailed mechanism that involved only these 58 species was retained in the simplified mechanism. Ignition delay times were calculated using the simplified mechanism and the detailed mechanism at conditions similar to those employed in the shock-tube experiments. At all conditions the differences were found to be less than 14%.

Figure 7 shows the mass fraction of toluene in the fuel stream at extinction, $Y_{F,1}$, as a function of the strain rate, $a_{2,e}$. The symbols represent measurements. The solid line represents results of numerical calculations performed using the simplified chemical-kinetic mechanism. At a given value of $Y_{F,1}$ the calculated value of $a_{2,e}$ is lower than that measured. Figure 8 shows the oxidizer temperature at autoignition, as a function of the strain rate, $a_{2,I}$. The symbols represent measurements reproduced from Refs. [11, 27]. The solid line represents results of numerical calculations performed using the simplified chemical-kinetic mechanism. At a given value of the oxidizer temperature the calculated value of $a_{2,I}$ is lower than that measured. Thus in both extinction and ignition experiments, the numerical model predicts that toluene/air is overall less reactive than observed in the experiments. This result is consistent with comparisons between the model predictions and experimental results from the shock tube

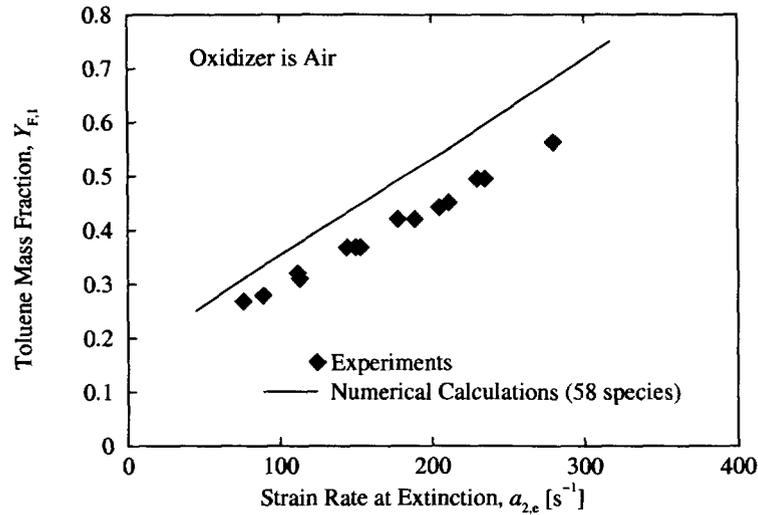


Figure 7: Mass fraction of toluene in the fuel stream at extinction, $Y_{F,1}$, as a function of the strain rate, $a_{2,e}$. The symbols represent measurements. The solid line represents results of numerical calculations performed using the simplified chemical-kinetic mechanism made up of 58 species.

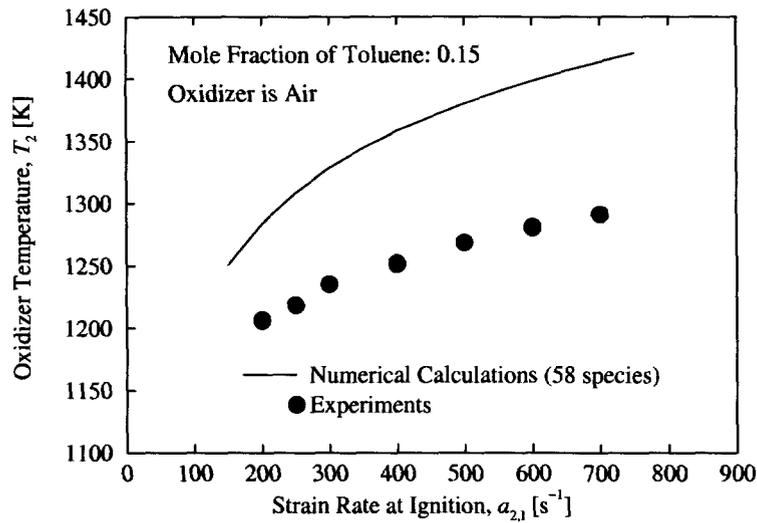


Figure 8: Oxidizer temperature at autoignition, $T_{2,I}$, as a function of the strain rate, $a_{2,I}$. The symbols represent measurements [11, 27]. The solid line represents results of numerical calculations performed using the simplified chemical-kinetic mechanism made up of 58 species.

above 1400K.

The sensitivity results for autoignition under nonpremixed conditions are given in Fig. 9. The analysis performed by FlameMaster [24] gives the change in maximum OH concentration

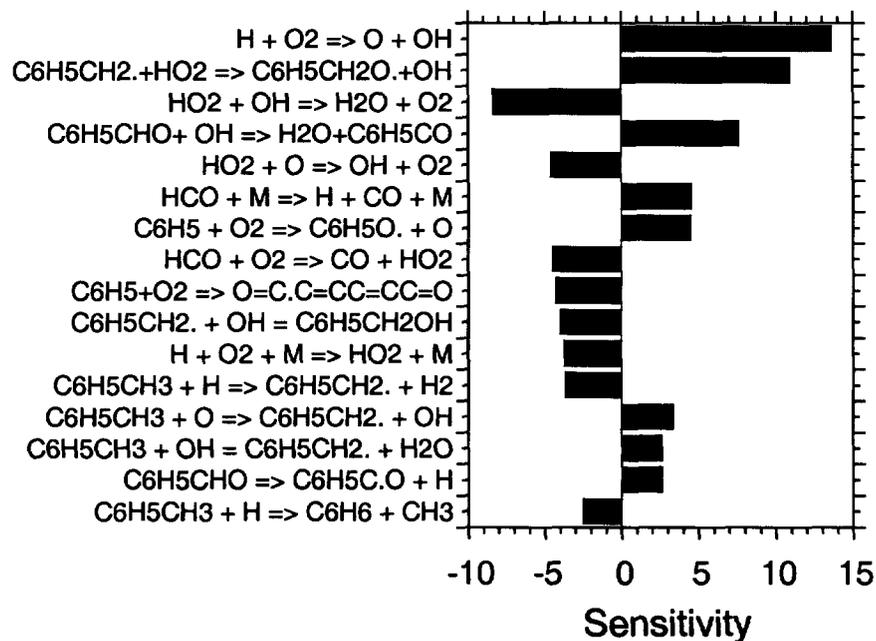
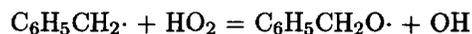


Figure 9: Sensitivity of the OH radical concentration to changes in individual rate constants under nonpremixed conditions near autoignition (strain rate = 400 s^{-1} , oxidizer temperature $T_2 = 1357 \text{ K}$).

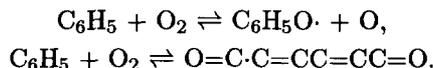
for an incremental change in rate constant as indicated in Fig. 9. In FlameMaster, forward and reverse rate constants are considered as separate parameters for the purposes of sensitivity analysis. The analysis was performed for a reactive flow solution very near autoignition. Positive sensitivities indicate an increase in rate constant increases the OH concentration and accelerates the overall rate of reaction, while negative sensitivities indicate an increase in rate constant decreases the OH concentration and retards the overall rate of reaction. The $H + O_2$ chain branching reaction again gives very high sensitivity as under shock tube and flow reactor conditions. The reaction benzyl radicals with HO_2 ,



exhibits a particularly high sensitivity under counterflow ignition conditions. The reaction of

benzaldehyde with OH shows a high positive sensitivity and promotes ignition.

The reactions that give significant sensitivity under nonpremixed conditions but not under flow reactor or shock tube conditions are reactions that involve the phenyl + O₂ reaction:



An important uncertainty in the phenyl + O₂ system is the branching ratio between the two product channels given above. The O-atom product channel is accelerating and the other ring-opening product channel is retarding (Fig. 9). The branching ratio depends on the relative barrier heights for the phenylperoxy radical going to O-O bond breakage versus to ring opening [19].

Conclusions

The detailed chemical-kinetic model for toluene was improved by adding a more accurate description of the phenyl + O₂ reactions, toluene decomposition reactions and the benzyl radical + O reaction. These reactions have been analyzed by quantum RRK to obtain $k(E)$ and by master equation for fall-off. New data obtained under nonpremixed conditions in a counterflow configuration and obtained in a shock tube were compared to results of the detailed chemical-kinetic model. Sensitivity analysis was used to identify reactions whose rate constants control the overall rate of oxidation. This information can be used to obtain future improvements of the agreement between the model and experiments. The reactions that exhibited high sensitivity (besides H + O₂ chain branching) included toluene decomposition reactions, toluene reaction with H, OH and O₂, and benzyl reaction with HO₂ and O₂. Also, phenyl + O₂ reactions were shown to be important during ignition in a nonpremixed, counterflow system. Although the benzyl + O reaction did not appear in the sensitivity analysis, it was primary reaction consuming benzyl under shock tube and flow reactor conditions.

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